Physical Chemistry Chemical Physics 2015 vol.17 N27, pages 18063-18071

The puzzling first-order phase transition in water-glycerol mixtures

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Abstract

© the Owner Societies 2015. Over the last decade, discussions on a possible liquid-liquid transition (LLT) have strongly intensified. The LLT proposed by several authors focused mostly on explaining the anomalous properties of water in a deeply supercooled state. However, there have been no direct experimental observations yet of LLT in bulk water in the so-called 'no man's land', where water exists only in the crystalline states. Recently, a novel experimental strategy to detect LLT in water has been employed using water-glycerol (W-G) mixtures, because glycerol can generate a strong hindrance for water crystallization. As a result, the observed first-order phase transition at a concentration of glycerol around cg ≈ 20 mol% was ascribed to the LLT. Here we show unambiguously that the first order phase transition in W-G mixtures is caused by the ice formation. We provide additional dielectric measurements, applying specific annealing temperature protocols in order to reinforce this conclusion. We also provide an explanation, why such a phase transition occurs only in the narrow glycerol concentration range. These results clearly demonstrate the danger of analysis of phase-separating liquids to gain better insights into water dynamics. These liquids have complex phase behavior that is affected by temperature, phase stability and segregation, viscosity and nucleation, and finally by crystallization, that might lead to significant misinterpretations.

http://dx.doi.org/10.1039/c5cp02851e